MANUFACTURE OF A GAS DIFFUSION ELECTRODE

5   The present invention relates to a process for the manufacture of an electrode, wherein the electrode is suitable for use as a component of a fuel cell membrane electrode assembly.

Electrochemical cells invariably comprise at their fundamental level a solid or
10 liquid electrolyte and two electrodes, the anode and cathode, at which the desired electrochemical reactions take place. A fuel cell is an energy conversion device that efficiently converts the stored chemical energy of a fuel and an oxidant into electrical energy. The fuel is usually hydrogen, stored as a gas, or methanol stored as a liquid or gas, and the oxidant is air or oxygen. The hydrogen or methanol is oxidised at the anode
15 and the oxygen is reduced at the cathode. In these cells gaseous reactants and/or products have to be diffused into and/or out of the cell electrode structures. The electrodes therefore are specifically designed to be porous to gas and/or liquid diffusion in order to optimise the contact between the reactants and the reaction sites in the electrode to maximise the reaction rate. The electrolyte which has to be in contact
20 with both electrodes to maintain electrical contact in the fuel cell may be acidic or alkaline, liquid or solid, in nature. In the proton exchange membrane fuel cell (PEMFC), whether hydrogen or methanol fuelled, the electrolyte is a solid proton conducting polymer membrane, commonly based on perfluorosulphonic acid materials. The PEMFC is the most likely type of fuel cell to find wide application as a more
25 efficient and lower emission power generation technology in a range of markets including stationary and portable power devices and as alternative to the internal combustion engine in transportation.

In the PEMFC the combined laminate structure formed from the membrane and
30 the two electrodes is known as a membrane electrode assembly (MEA). The MEA will typically comprise several layers, but can in general be considered, at its basic level, to have five layers, which are defined principally by their function. On either side of the membrane an anode and cathode electrocatalyst is incorporated to increase the rates of the desired electrode reactions. In contact with the electrocatalyst containing layers, on
35 the opposite face to that in contact with the membrane, are the anode and cathode gas

diffusion substrate substrates (GDS). The anode GDS is designed to be porous and to allow the reactant hydrogen or methanol to enter from the face of the substrate exposed to the reactant fuel supply, and then to diffuse through the thickness of the substrate to the layer which contains the electrocatalyst, usually platinum metal based, to maximise

5 the electrochemical oxidation of hydrogen or methanol. If the reactant is methanol, the anode GDS must also allow carbon monoxide to escape. The cathode GDS is also designed to be porous and to allow oxygen or air to enter the substrate and diffuse through to the electrocatalyst layer reaction sites. Additionally, the cathode GDS must allow product water to be removed.

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The complete MEA can be constructed by several methods. The electrocatalyst layers can be bonded to one surface of the GDS to form what is known as a gas diffusion electrode (GDE). The MEA is then formed by bonding two GDEs with the solid proton-conducting membrane. Alternatively, the MEA may be formed from two porous GDSs

15 and a solid proton-conducting polymer membrane catalysed on both sides (hereinafter referred to as a catalyst coated membrane or CCM); or indeed the MEA may be formed from one GDE and one GDS and a solid proton-conducting polymer catalysed on the side facing the GDS.

20   The electrocatalyst materials for the anode and cathode structures typically comprise precious metals, in particular platinum, as these have been found to be the most efficient and stable electrocatalysts for all low-temperature fuel cells such as the PEMFC. Platinum is employed either on its own as the only electrocatalyst metal or in combination with other precious metals or base metals. The platinum based

25 electrocatalyst is provided as very small particles (~20-50Å) of high surface area, which are often distributed on and supported by larger macroscopic electronically conducting carbon particles to provide a desired catalyst loading. Conducting carbons are the preferred materials to support the catalyst. Particulate carbon black materials typically employed include Vulcan XC72R and Shawinigan. It is also possible that the platinum

30 based electrocatalyst may not incorporate a support, and in this case it is referred to as an unsupported Pt electrocatalyst.

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The electrocatalyst layers suitably comprise some level of the proton conducting polymer in contact with the electrocatalyst reaction sites. This enables the efficient transport of protons from the anode reaction sites through the polymer membrane to the cathode reaction sites.

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One method of incorporating proton conducting polymer into an electrocatalyst layer is a method wherein a catalyst layer is applied to a GDS, and a solution of proton conducting polymer is subsequently applied to the catalyst layer. The electrocatalyst is formulated into a catalyst ink by dispersing in water and adding a suitable binder. 10 The catalyst ink is applied to the GDS by a suitable process such as screen printing or spraying. Thereafter a solution of proton conducting polymer is applied to the electrocatalyst layer. Such processes are described in EP 577 291.

By incorporating proton conducting polymer in the catalyst layer, it is possible to 15 improve catalyst utilisation wherein the proportion of the platinum-based catalyst that actually takes part in the catalytic reaction is increased. The catalyst utilisation is affected by the three-phase interface between the catalyst, the gaseous reactants, and the proton-conducting polymer. Improving the catalyst utilisation can increase the MEA performance (measured as cell voltage at a given current density) without increasing the 20 amount of platinum-based catalyst.

The problem of improving catalyst utilisation is addressed in EP 637 851. A colloidal dispersion of proton conducting polymer is mixed with a supported catalyst and applied to a GDS to produce a catalyst layer. The colloidal dispersion contains an 25 organic solvent with a polar group other than hydroxyl, eg an ester, ether, carbonyl, amino or carboxyl group.

The present inventors have sought to find alternative methods of producing catalyst layers with high catalyst utilisation.

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Accordingly, the present invention provides a process for the manufacture of a gas diffusion electrode comprising the steps of

    a) application of a catalyst ink to a gas diffusion substrate;

b) firing;

c) application of a proton-conducting polymer solution; and

d) drying;

characterised in that the proton-conducting polymer solution comprises one or more

5 solvents selected from the group of solvents with structure A

$$R^1 \overset{\displaystyle \overset{O}{\parallel}}{\underset{}{C}} \overset{}{\underset{N}{\underset{\displaystyle |}{}}} \overset{R^2}{\underset{R^3}{}} \qquad A$$
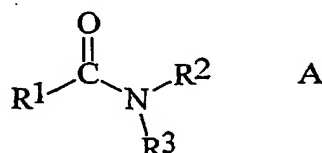
wherein R^1, R^2 and R^3 are independently chosen from H, methyl, ethyl, n-propyl and iso-propyl.

10   Suitably, the proton-conducting polymer solution comprises one or more solvents selected from N,N-dimethylacetamide, N,N-diethylacetamide, formamide, N-methylformamide, N,N-dimethylformamide, N-ethylacetamide, N,N-dipropylacetamide and N-methyl, N-ethylacetamide.

15   Preferably,   the   proton-conducting   polymer   solution   comprises N,N-dimethylacetamide (R^1, R^2 and R^3 are methyl).

The catalyst ink suitably comprises an electrocatalyst, a solvent, optionally one or more binders and optionally one or more rheology modifiers. In one embodiment of the

20 invention, the electrocatalyst is an unsupported metal catalyst such as platinum black. In a second embodiment of the invention, the electrocatalyst is a supported metal catalyst, such as platinum or a platinum alloy supported on a conductive carbon support. The metal catalyst is dispersed in a solvent, preferably water. Suitable binders include hydrophobic polymers such as polytetrafluoroethylene (PTFE) or fluorinated ethylene-

25 propylene (FEP).   Rheology modifiers are suitably cellulose-based, such as methylcellulose.

The catalyst ink may be applied to a GDS using any technique known to those skilled in the art. Suitable techniques include screen printing, spraying, K-bar techniques

30 and doctor blade methods.

The GDS is made of porous electrically conductive sheet material. Suitable materials include carbon fibre papers, for example those available from Toray Industries, Japan, (Toray TGP-H-60 or TGP-H-90), and woven carbon fibre cloths, for example those available from Zoltek Corporation, USA, (Zoltek PWB-3). Substrates such as

5 these are usually modified with a particulate material either embedded within the fibre network or coated on to the large planar surfaces, or a combination of both. Typically these particulate materials comprise a carbon black and polymer mix. The particulate carbon black material is, for example, an oil furnace black such as Vulcan XC72R (from Cabot Chemicals, USA) or an acetylene black such as Shawinigan (from Chevron

10 Chemicals, USA). The polymer most frequently used is polytetrafluoroethylene (PTFE). The coating, or embedding, is carried out in order to improve the water management properties, improve gas diffusion characteristics, to provide a continuous surface on which to apply the catalyst layer and to improve the electrical conductivity. An alternative material that has shown comparable performance to carbon paper or cloth is a

15 substrate comprising a non-woven network of carbon fibres (carbon fibre structures such as Optimat 203, from Technical Fibre Products, UK) with a particulate material embedded within the fibre network. Such materials are disclosed in EP 0 791 974, WO 00/47816, WO 00/55933 and EP 1 063 716.

20   The firing step (b) is suitably carried out in air and must be carried out at a temperature that is sufficient to burn off any rheology modifiers that have been incorporated into the catalyst ink. The temperature must also be sufficient to cause any polymer binders such as PTFE to flow. A suitable firing temperature for a catalyst layer comprising PTFE is in the range 300-400°C.

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      The proton-conducting polymers suitable for use in the present invention may include, but are not limited to:
      1) Polymers which have structures with a substantially fluorinated carbon chain optionally having attached to it side chains that are substantially fluorinated. These

30 polymers contain sulphonic acid groups or derivatives of sulphonic acid groups, carboxylic acid groups or derivatives of carboxylic acid groups, phosphonic acid groups or derivatives of phosphonic acid groups and/or mixtures of these groups. Perfluorinated polymers include Nafion®, Flemion® and Aciplex® commercially available from E. I.

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DuPont de Nemours (U.S. Patents 3,282,875; 4,329,435; 4,330,654; 4,358,545; 4,417,969; 4,610,762; 4,433,082 and 5,094,995), Asahi Glass KK and Asahi Chemical Industry respectively. Other polymers include those covered in U.S. Patent 5,595,676 (Imperial Chemical Industries plc) and U.S. Patent 4,940,525 (Dow Chemical Co.).

5   2) Perfluorinated or partially fluorinated polymers containing aromatic rings such as those described in WO 95/08581 and WO 97/25369 (Ballard Power Systems) which have been functionalised with SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2. Also included are radiation or chemically grafted perfluorinated polymers, in which a perfluorinated carbon chain, for example, PTFE, fluorinated
10 ethylene-propylene (FEP), tetrafluoroethylene-ethylene (ETFE) copolymers, tetrafluoroethylene-perfluoroalkoxy (PFA) copolymers, poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVDF) is activated by radiation or chemical initiation in the presence of a monomer, such as styrene, which can be functionalised to contain an ion exchange group.

15   3) Fluorinated polymers such as those disclosed in EP 0 331 321 and EP 0 345 964 (Imperial Chemical Industries plc) containing a polymeric chain with pendant saturated cyclic groups and at least one ion exchange group which is linked to the polymeric chain through the cyclic group.

      4) Aromatic polymers such as those disclosed in EP 0 574 791 and US Patent
20 5,438,082 (Hoechst AG) for example sulphonated polyaryletherketone. Also aromatic polymers such as polyether sulphones which can be chemically grafted with a polymer with ion exchange functionality such as those disclosed in WO 94/16002 (Allied Signal Inc.).

      5) Nonfluorinated polymers include those disclosed in U.S. Patent 5,468,574
25 (Dais Corporation) for example hydrocarbons such as styrene-(ethylene-butylene)-styrene, styrene-(ethylene-propylene)-styrene and acrylonitrile-butadiene-styrene co- and terpolymers where the styrene components are functionalised with sulphonate and/or phosphonic groups.

      6) Nitrogen containing polymers including those disclosed in U.S. Patent
30 5,599,639 (Hoechst Celanese Corporation), for example, polybenzimidazole alkyl sulphonic acid and polybenzimidazole alkyl or aryl phosphonate.

The proton-conducting polymer solution comprising one or more of the solvents of structure A may be produced by a solvent exchange technique. Proton-conducting polymers may be purchased as solutions in a mixture of alcohols and water, eg EW1100 5% Nafion® solution available from DuPont. The solvent exchange technique can be used if the solvents of structure A have higher boiling points than the solvents in the as-purchased solution. The solvents of structure A, eg N,N-dimethylacetamide, are added to the as-purchased solution, and the lower boiling point solvents are evaporated. This may be carried out using a rotary evaporator or a fractionating column.

The proton-conducting polymer solution comprising one or more of the solvents of structure A may also be produced by dissolving a polymer in the appropriate solvent, preferably in an autoclave.

The proton-conducting polymer solution may be applied to the fired catalyst layer by techniques such as screen printing, spraying, K-bar methods or doctor blade techniques. A preferred technique is screen printing.
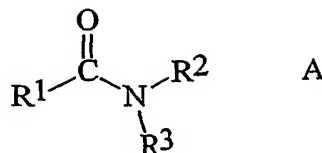
After the proton-conducting polymer solution has been applied, the catalyst layer is dried to remove solvent from the catalyst layer. This can be carried out in an oven with or without a vacuum. A suitable drying temperature is in the range of 100-130°C.

The present invention further provides a novel process for the manufacture of an MEA comprising the steps of

a) application of a catalyst ink to a gas diffusion substrate to form a gas diffusion electrode;

b) firing the gas diffusion electrode;

c) application of a proton-conducting polymer solution to the gas diffusion electrode;

d) optionally drying the gas diffusion electrode; and

e) combining the gas diffusion electrode with a proton conducting polymer membrane;

characterised in that the proton-conducting polymer solution comprises one or more solvents selected from the group of solvents with structure A

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$$R^1 - \overset{\overset{\displaystyle O}{\|}}{C} - \underset{\underset{\displaystyle R^3}{|}}{N} - R^2 \qquad A$$

wherein R^1, R^2 and R^3 are independently chosen from H, methyl, ethyl, n-propyl and iso-propyl.

5   Suitably, the proton-conducting polymer solution comprises one or more solvents selected from N,N-dimethylacetamide, N,N-diethylacetamide, formamide, N-methylformamide, N,N-dimethylformamide, N-ethylacetamide, N,N-dipropylacetamide and N-methyl, N-ethylacetamide.

10   Preferably, the proton-conducting polymer solution comprises N,N-dimethylacetamide (R^1, R^2 and R^3 are methyl).

Preferably, two GDEs are combined with the proton conducting polymer membrane. To combine the electrodes and the membrane, it is preferred to use a
15 laminating process wherein the components are combined by the application of pressure, and optionally heat. Suitable MEA laminating processes are described in EP 577 291. The drying step (d) is optional because in one embodiment of the invention, the membrane and the GDE can be combined whilst the GDE is still wet, ie solvent is still present in the catalyst layer. If the lamination step is carried out using a wet GDE, it
20 may be necessary to dry the MEA after lamination, in order to remove any residual solvent.

It is particularly appropriate to leave out drying step (d) and combine the membranes and GDE whilst the GDE is still wet if the membrane has a high glass-
25 transition temperature (T_g). Certain polyaromatic polymers such as sulphonated polyaryl ether polymers are used as polymer electrolyte membranes and have a very high T_g. They may be combined with electrodes containing lower T_g polymers such as perfluorinated sulphonic acid polymers. If the lamination step is not carried out under "wet" conditions, the polymer membrane may decompose or the temperature may be too

low so that the polymer membrane will not flow, and an effective bond between polymer in the membrane and polymer in the electrode will not be formed.

The proton-conducting polymer membrane may contain the same proton-conducting polymer as the proton-conducting polymer solution that is applied to the catalyst layer. However, the proton-conducting polymers in the membrane and the solution that is applied to the catalyst layer may be different.

The electrodes and MEAs manufactured according to the processes of the invention are suitable for use in fuel cells, but may also find use in other applications such as gas sensors or electrolytic reactors. The electrodes and MEAs comprising unsupported catalysts may be particularly useful when used in Direct Methanol Fuel Cells.

The invention will now be described by way of example only.

Comparative Example 1

Electrode preparation: Two carbon fibre paper substrates (Toray TGP-H-60) were treated with PTFE, and carbon black base layers were applied to one surface of each substrate. Platinum black catalyst layers were printed onto the base layers at a loading of 4.19mg/cm^2. The layers were fired at 385°C in air for 16 minutes. A top-coat of ion-conducting polymer solution was brushed onto each catalyst layer. The polymer solution was an aqueous solution of Nafion®, produced as described in EP 731 520 and essentially containing water and 10wt% Nafion® polymer. The polymer coatings were dried at 105°C in air to remove the water, giving a polymer loading of 0.23mg/cm^2.

MEA preparation: The two electrodes were combined with a Nafion 112 membrane (DuPont) in a standard MEA lamination process, as commonly practised in the art.

Comparative Example 2

Electrodes and an MEA were prepared as in example 1 except the loading of the Nafion® polymer on each electrode was 0.7mg/cm^2.

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EXAMPLE 1

Electrode preparation: A first electrode was prepared as described in comparative example 1. A second electrode was prepared in a similar manner except
10 that the ion-conducting polymer solution was a 10wt% solution of Nafion® polymer in N,N-dimethylacetamide. The solution was produced by a solvent exchange process using as-received EW1100 Nafion® solution from DuPont. The solution was brushed onto the platinum black catalyst layer and dried at 105°C in air, giving a polymer loading of 0.32mg/cm^2. A second coat of the solution was brushed onto the electrode, but the
15 second layer was not dried. This gave a wet electrode with a nominal polymer loading of 0.6mg/cm^2.

MEA preparation: The first and second electrodes were combined with a Nafion 112 membrane (DuPont) as in comparative example 1. The second electrode was wet (ie
20 N,N-dimethylacetamide solvent remained in the catalyst layer) when the MEA was bonded. After the lamination step, the MEA was dried at 105°C to remove any remaining solvent.

MEA Performance

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The MEAs produced in comparative examples 1 and 2 and example 1 were tested in a fuel cell at 80°C. Hydrogen at 200kPa gauge and 100% relative humidity was supplied to the anode, and air or oxygen at 200kPa gauge and 100% relative humidity was supplied to the cathode. The reactant stoichiometry was 1.5:2 for hydrogen to air
30 and 1.5:10 for hydrogen to oxygen (giving the same volumetric gas flow rate in both cases).

Figure 1 shows the cell voltage versus the current density for the three MEAs. There are two data sets for example 1. In a first experiment, the second electrode (made using the N,N-dimethylacetamide solution) was placed on the cathode side of the fuel cell. The data from this experiment is simply labelled "Example 1: Air/Oxygen". In a

5 second experiment, the second electrode was placed on the anode side of the fuel cell. The data from this experiment is labelled "Example 1 reversed: Air/Oxygen". Under the conditions in the performance test (with a pure hydrogen feed) it is the cathode that limits the performance of an MEA. If the catalyst utilisation in the cathode is improved, there will be a marked improvement in the MEA performance, particularly at low current

10 densities.

Figure 1 shows that the performance of comparative example 1 and "example 1 reversed" are comparable. There is no performance benefit gained by placing the electrode made using the N,N-dimethylacetamide solution at the anode side of the fuel

15 cell. Comparative example 2 has a higher Nafion® loading than comparative example 1, but shows similar performance at low current densities and therefore the catalyst utilisation is not significantly altered by the increased polymer loading. Example 1 exhibits the best performance at low current densities. Placing the electrode made using the N,N-dimethylacetamide solution at the cathode side of the fuel cell produces a

20 performance gain, demonstrating that the use of the N,N-dimethylacetamide solution improves the catalyst utilisation in the catalyst layer.